Chemistry

Lecture 5 By: Syed Ali Shan

Aldehydes and Ketones

Outline:

- Nomenclature
- Preparation
- Reactivity

Nomenclature

Common Names of Ketones:

- If **R** groups are same, use di as prefix i.e. CH_3COCH_3 is Dimethyl ketone.
- If **R** groups are different, name them alphabetically i.e. $C_2H_5COCH_3$ is Ethyl methyl ketone.

IUPAC Rules for Ketones:

Selection of Chain:

- Select the longest continuous carbon chain containing carbonyl group.
- If more than one chain is of same length, then select one with maximum no. of carbonyl groups.
- If no. carbonyl groups is same, select one with maximum substituents and if substituents are also same, then select any.

Numbering:

- Start numbering from the end nearer to carbonyl group and if carbonyl group is at same distance from both ends, start numbering from end nearer to substituent.
- If substituent is also at same distance, then start numbering from either end.

Naming:

- Name alkane is replaced with “alkanone”.
  Position of substituent-name of substituent-position of carbonyl carbon-alkanone
- If more than one carbonyl groups are present then use dione, trione etc.

Common Names of Aldehydes:

- Common names of aldehydes are to be remembered.

IUPAC Rules for Aldehydes:

Selection of Chain:

- Select the longest continuous carbon chain containing carbonyl group.
- If more than one chain is of same length, then select one with maximum no. of carbonyl groups.
- If no. carbonyl groups is same, select one with maximum substituents and if substituents are also same, then select any.

Numbering:

- Start numbering from the end of carbonyl group.

Naming:

- Name alkane is replaced with "alkanal".
  Position of substituent-name of substituents alkanal
- If two carbonyl groups are present then use dial.

Structure of Aldehydes and Ketones

- Aldehydic group is present sugar and constituent of essential oils
- Ketonic group is present in camphor and menthone
- General formula for both is $\mathbf{C_nH_{2n}O}$
- Formyl group (-CHO) is the functional group in aldehydes
- Carbonyl group ($>C=O$) is the functional group in ketones
- Both carbon and oxygen of carbonyl group are sp2 hybridized (planner triangular)
- Carbonyl carbon acts as electrophilic centre
- Oxygen acts as nucleophilic centre
- Pi bond b/w carbon and oxygen is distorted towards oxygen (high E.N)
- This distortion induces polarity
- **Isomerism;**
  - Aldehydes and ketones are functional group isomers of each other
  - Aldehydes can show chain, functional group and tautomerism
  - Ketones can show all structural isomerisms
- **Physical properties;**
  - Methanal is only carbonyl compound existing in gas phase
  - Propanone is first and simplest ketone
  - Lower aldehydes and ketones are soluble in water
  - M.P and B.P increases with carbon chain

Carboxylic acids/alcohols(H-bonding) > Ald./Ket.(Dipole forces) > Alkane(London forces)

Preparation of Aldehydes and Ketones

Generally:

1^0 Alcohols $\xrightarrow{[O]}$ Aldehydes

2^0 Alcohols $\xrightarrow{[O]}$ Ketones

Preparation of Methanal (Formaldehyde):

- **Laboratory:**

$$2CH_3OH + O_2 \xrightarrow[300^0C]{\text{Cu or Pt}-\text{asbestos}} 2HCHO + 2H_2O$$

- **Industrial:**

$$2CH_3OH + O_2 \xrightarrow[500^0C]{FeO + Mo_2O_3} 2HCHO + 2H_2O$$

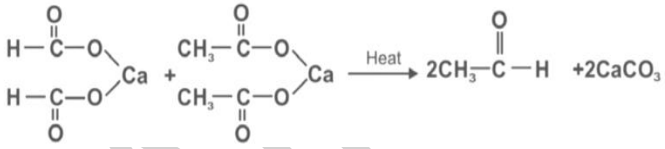
Formalin: 40 % formaldehyde (methanal) + 52 % water + 8 % methanol

Preparation of Ethanal (Acetaldehyde):

- **Laboratory:**

$$C_2H_5OH + [O] \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} CH_3CHO + H_2O$$

Calcium salts of acetic acid and formic acid on dry distillation yield ethanal

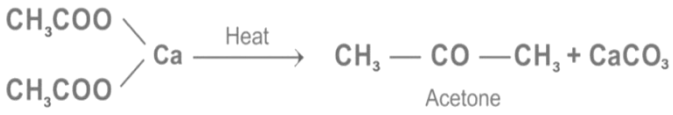


- **Industrial:**

$$2CH_2{=}CH_2 + O_2 \xrightarrow[CuCl_2\ (promotor)]{PdCl_2(catalyst)} 2CH_3CHO$$

Preparation of Acetone:

- By dry distillation of calcium acetate



Reactions of Aldehydes and Ketones along Mechanisms

Reactivity:

- Prefer nucleophilic addition reactions
- Also undergo redox reactions
- Aldehydes are more reactive than ketones as;
  - ☞ Greater steric hinderance in ketones due to bulky groups resulting difficult attack of Nu)
  - ☞ Alkyl groups are electron donating, making carbonyl carbon less electrophilic
  - ☞ Methanal is the most reactive among carbonyl compounds
  - ☞ Methanal > Ethanal > Propanal > Propanone
- Increase in alkyl chain;
  - ☞ Increases steric hinderance
  - ☞ Decreases polarity

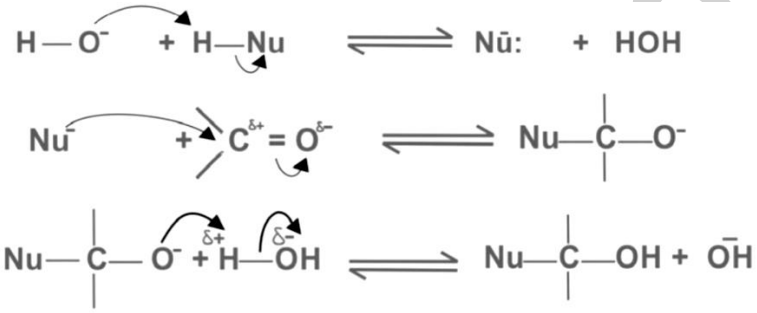
- ☞ Decreases reactivity
- ☞ Increases stability

- Both ald./ket. give addition products (Adducts)

(A) Base Catalysed Reactions:

General Mechanism:

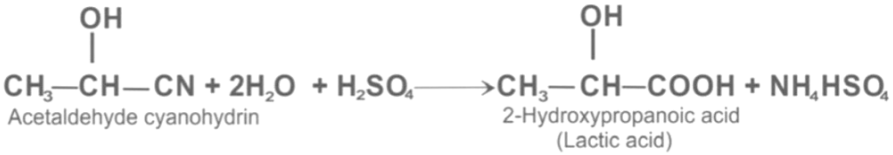
- Base increases the nucleophilic character of attacking reagent
- Mechanism is initiated by strong nucleophile (of attacking reagent) generated with help of the strong base
- Nucleophile attacks the carbonyl carbon



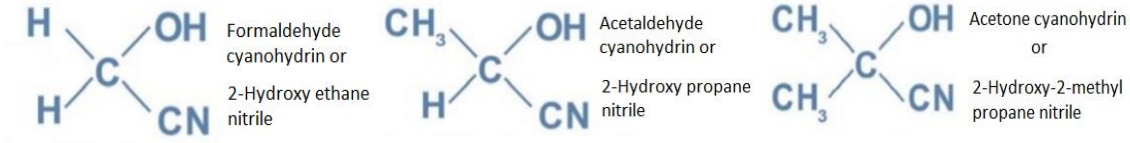
1. **With Hydrogen Cyanide (HCN):**
   - Products are called cyanohydrins or hydroxy nitriles

Mechanism:

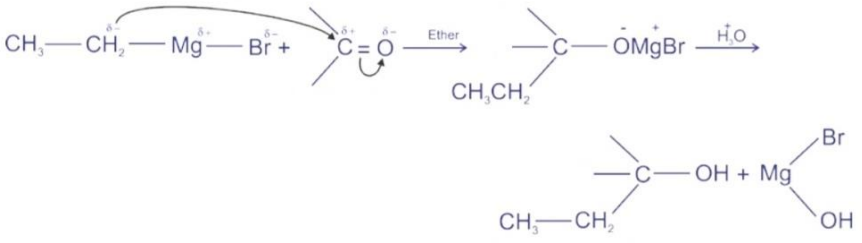
- CN^- is nucleophile and is involved in rate determining step
- Acid hydrolysis of –CN produces –COOH i.e nitriles produce carboxylic acid through acid amide (intermediate)



Important Names:



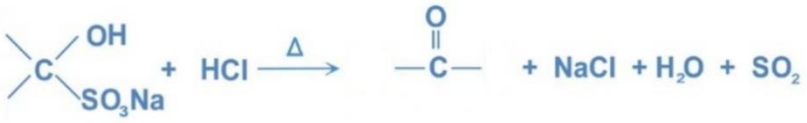
2. **With Grignard Reagent (RMgX):**



- Only methanal gives primary alcohol with Grignard reagent
- All other aldehydes give secondary alcohols with Grignard reagent
- All ketones give tertiary alcohols with Grignard reagent

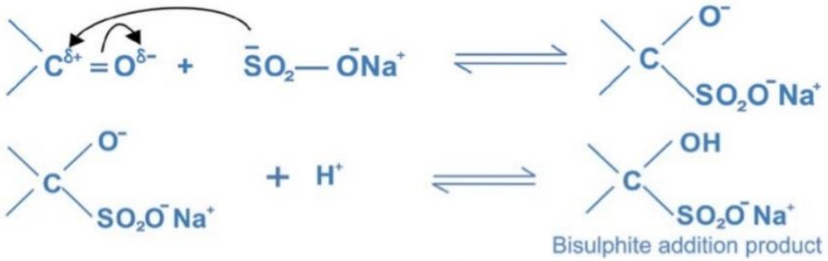
3. **With Sodium Bisulphite ($NaHSO_3$):**
   - Give bisulphite addition products
   - Aldehydes and small methyl ketones give white ppt.
   - Used to distinguish between carbonyl and non carbonyl compounds
   - Used to purify, separate carbonyl compounds from rest

   - Carbonyl compounds are recovered using dilute mineral acid like HCl

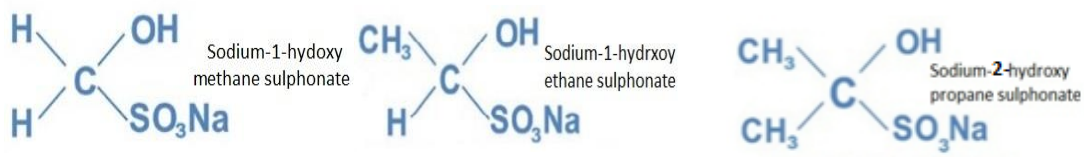


Mechansim:

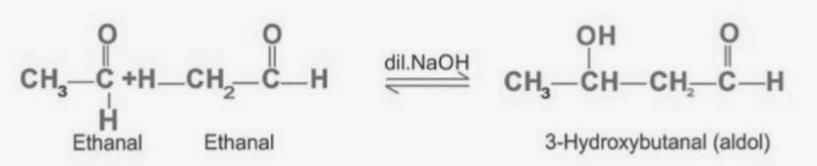
The sulphite ion acts as a nucleophile, since the sulphur atom is more nucleophilic than oxygen, a C—S bond is formed.

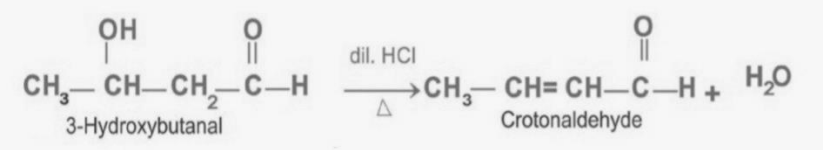


Important Names:



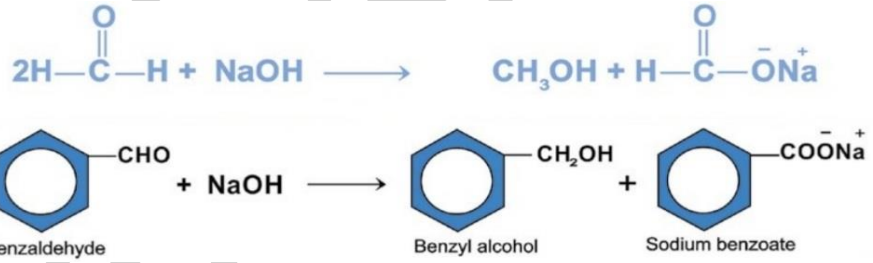
4. **Aldol Condensation:**
    - Aldehydes and ketones possessing α-hydrogen give this reaction
    - React with dilute base
    - Product are called aldol (due to aldehydic and hydroxyl groups)



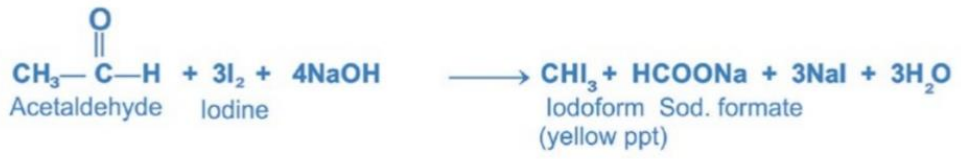


Mechanism: Only see from text book

5. **Cannizzaro's Reaction:**
    - Aldehydes and ketones possessing no α-hydrogen give this reaction
    - React with conc. Base i.e. 50 % NaOH
    - It is disproportionation (self oxidation reduction) reaction
    - Alcohol (result of reduction) and salt of carboxylic acid (result of oxidation)



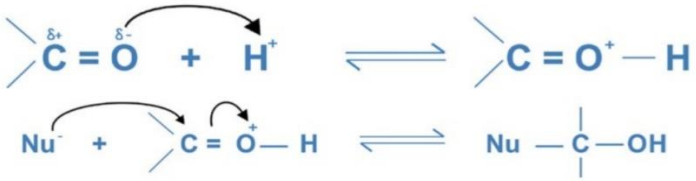
6. **Haloform Reaction:**
    - Aldehydes and ketones having at least one $-CH_3$ group attached to carbonyl carbon give this reaction **or** aldehydes and ketones having acetyl group
    - Only I_2/NaOH give coloured ppt. i.e. CHI_3 (iodoform) [two steps mechanism]
    - Only acetaldehyde among aldehydes give this test (iodoform test)
    - Methyl ketones give this test
    - One carbon of carbonyl compound changes to iodoform while rest form salt



(B) Acid Catalysed Reactions:

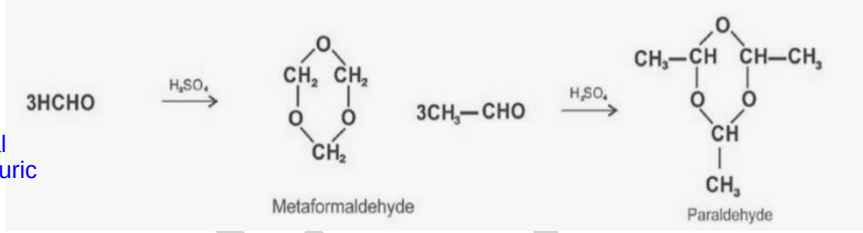
General Mechanism:

- Acid increases the electrophilic character of carbonyl carbon
- Mechanism is initiated by proton released by acid by attacking O-atom of carbonyl group

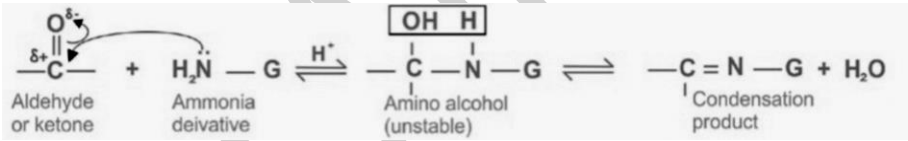


1. **With dil. H_2SO_4:**

Only methanal and ethanal form stable ring with sulphuric acid.

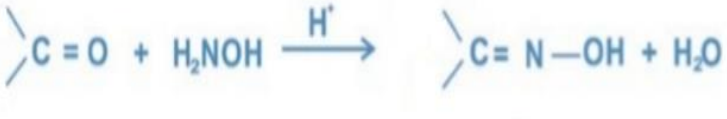


2. **With Ammonia Derivatives:**



- This is called condensation or addition-elimination reaction
- Loss of carbonyl oxygen
- "G" can be –OH, $–NH_2$, $–NHC_6H_5$, $–NHCONH_2$(formula of **semicarbazide☞$NH_2NHCONH_2$**), $–NHC_6H_3(NO_2)_2$

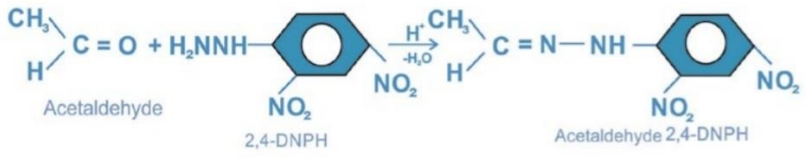
i. **With Hydroxylamine (NH_2-OH):**
   - Products are called oximes of each carbonyl compound



ii. **With Hydrazine (NH_2-NH_2):**

iii. **With Phenyl Hydrazine (NH_2-NHC_6H_5):**
   - Products in both are called hydrazones of each carbonyl compound

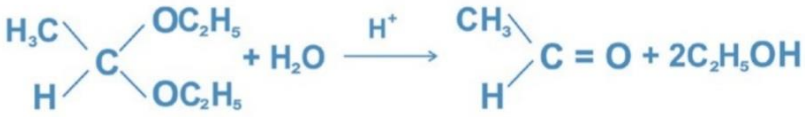
iv. **With 2,4-Dinitrophenyl Hydrazine (NH_2- $NHC_6H_3(NO_2)_2$) 2,4-DNPH:**
   - This is identification test for all carbonyl compounds
   - Products are called hydrazones (Brady's reagent)
   - Give orange red or yellow ppt



Mechanism: Only see from text book

Addition of Alcohols:

- Used to protect aldehydic group against oxidizing agents
- In presence Dry HCl
- Products are called acetals
- sp^2-hybridized carbon of carbonyl group changes sp^3 in acetal form
- Aldehydes can be recovered by hydrolyzing the acetals in presence of acid
- Ketones don't react in these conditions



Reduction Reactions:

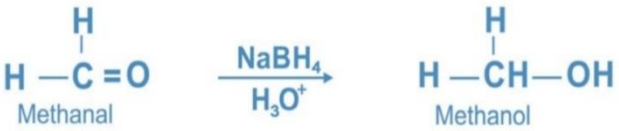
Mild Reducing agents:

- **$NaBH_4$, H_2/Ni** (partial reduction of ald./ket.) and **$LiAlH_4$** (partial reduction of carboxylic acids)
- Products are alcohols with same no. of carbons as in reactants

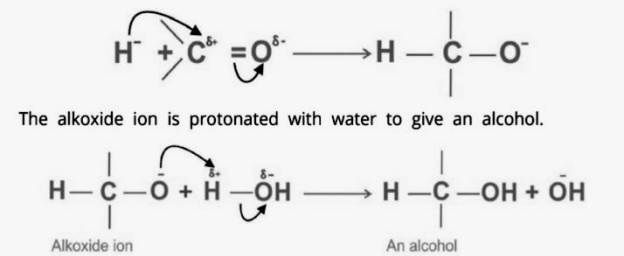
Strong Reducing agents:

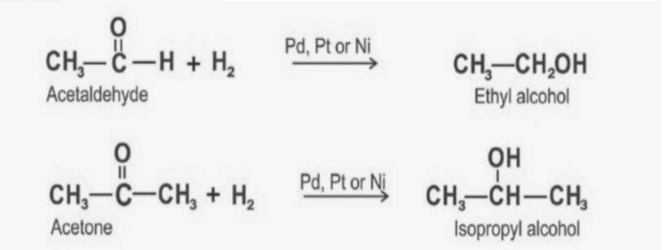
- **N_2H_4/KOH, Zn-Hg/HCl** (complete reduction of ald./ket.) and **HI/P** (complete reduction of carboxylic acids)
- Products are alkanes with same no. of carbons as in reactants

1. **With Sodium Borohydride ($NaBH_4$):**
   - Complex hydride
   - Source of H^- ions (hydride ion)
   - H^- act as nucleophile
   - It reduces C=O but not C=C or C-C
   - Aldehydes produce primary alcohols
   - Ketones produce secondary alcohols
   - Aldehydes and ketones are acting as oxidizing agents



Mechanism:





2. **With H_2/Ni (Catalytic Reduction):**
    - Ni or Pt or Pd are used as catalysts
    - Aldehydes produce primary alcohols
    - Ketones produce secondary alcohols
    - Aldehydes and ketones are acting as oxidizing agents

Oxidation Reactions:

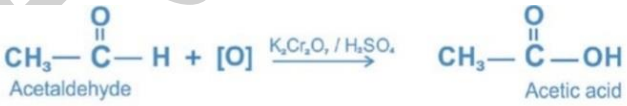
Mild Oxidzing agents:

- **Tollen's reagent , Benedict's solution** and **Fehling's solution**
- Only oxidize aldehydes to carboxylic acids

Strong Oxidizing agents:

- **$KMnO_4/H_2SO_4$, $K_2Cr_2O_7/H_2SO_4$** and **dil.HNO_3**
- Oxidize both aldehydes and ketones to carboxylic acids

1. **Oxidation of Aldehydes:**
    - Aldehydes are oxidized by both mild and strong oxidizing agents
    - No. of carbons atoms remain same during product formation
    - Only 1 molecule of carboxylic acid is produced



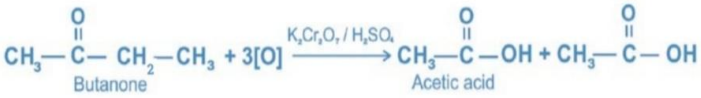
2. **Oxidation of Ketones:**
    - Ketones are only oxidized by strong oxidizing agents
    - Strong C-C bond is to be broken
    - Carbon attached to carbonyl carbon breaks its bond
    - 1 molecule of ketone produces 2 molecules of carboxylic acids(each with less no. of carbon atoms than ketone)

Oxidation of Symmetrical Ketones:

- Carbon bonded on either side of carbonyl carbon can break its bond

Oxidation of Unsymmetrical Ketones:

- Carbon atom possessing less H-atoms is preferentially oxidized and the carbonyl group remains with smaller alkyl group (Popoff's rule)



- Both aldehydes and ketones act as reducing agents in these reactions

Identification Tests:

- **2,4-DNPH test:** Both aldehydes and ketones give test
- **Sodium Bisulphite test:** Aldehydes and small methyl ketones give test
- **Tollen's Reagent test:** (silver mirror test)
  - Ammonical silver nitrate solution (alkaline and take part in redox reaction)
  - ($AgNO_3$ + NH_4OH) or $[Ag(NH_3)_2]^+OH^-$
  - Only aldehydes give silver ppt.

$$RCHO + 2[Ag(NH_3)_2]^+OH^- \rightarrow RCOONH_4 + 2Ag + 2NH_3 + H_2O$$

- **Fehling's Solution test:** (alkaline cupric tartrate solution)
  - Brick red ppt. of Cu_2O produced
  - Aliphatic aldehydes give test
- **Benedict's Solution test:** (alkaline cupric citrate solution)
  - Brick red ppt. of Cu_2O produced
  - Aliphatic aldehydes give test

$$R\text{-}CHO + 2Cu(OH)_2 + NaOH \rightarrow R\text{-}COONa + Cu_2O + 3H_2O$$

- **Sodium Nitroprusside test: $Na_2[Fe(CN)_5NO]$**
  - Ketones produce wine red or orange red colour